

## Tunable friction behavior of oriented carbon nanotube films

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Measured friction coefficients of carbon nanotubes vary widely from  $\mu < 0.1$ – $\mu > 1.0$  [1–6], while theoretical studies suggest intrinsically high friction coefficients, approaching unity [7]. Here we report that measured friction coefficients of MWNT films are strong functions of surface chemistry and temperature, but are not dependent on the presence of water vapor. We hypothesize that the origin of the temperature dependence arises from the interaction of the surface chemical groups on the nanotubes [8–12] and rubbing counterface. The friction coefficient of individual films can be easily tuned by changing the surface temperature and chemistry of either the countersurface or the nanotubes, we have demonstrated the ability to create and control high and low friction pairs through plasma treatments of the nanotube films with argon, hydrogen, nitrogen, and oxygen. This behavior is completely reversible, and when coupled with the superior strength, thermal, and electrical properties of nanotubes, provides a versatile tunable, multifunctional tribological system.

**KEY WORDS:** carbon nanotubes, coefficient of friction, micro-tribology, engineered surfaces

A schematic of the MWNT film grown with a vertical orientation is shown in figure 1 (a). Scanning electron microscopy images of a free edge of the vertical film are shown in figures 1(b)–1(d). The vertically aligned film was grown by a chemical vapor deposition (CVD) process using ferrocene and xylene precursors [13]. Following CVD growth, the MWNT films are cleaned using an oxygen plasma treatment. The vertically aligned MWNT films are approximately 65  $\mu\text{m}$  thick and 5% dense. The MWNTs were vertically aligned, with the last few micrometers from the top surface the films entangled and intertwined as shown in figures 1(b)–1(d). A sample of transversely orientated nanotubes was also prepared by mechanically removing the vertical MWNTs, sonicating in acetone and dispersing onto an identical quartz substrate. After drying, this transversely oriented nanotube film was found to be approximately 5  $\mu\text{m}$  thick and was comprised of a distributed ensemble of entangled nanotubes oriented in plane with the quartz substrate (figure 1(e) and 1(f)).

The mechanical, electrical, and thermal properties of individual nanotubes are highly anisotropic [14–18], and the frictional behavior was also recently found to be anisotropic [6]. These friction experiments used a countersurface made from a borosilicate glass pin (schematically shown in figure 2 (a)) and were run in a regime where wear was not observed. Under both inert gas and ambient conditions, the transversely distributed

films were repeatedly found to have friction coefficients  $\mu \sim 0.1$ , while the vertically aligned sample had  $\mu \sim 0.9$ . Molecular dynamics studies report nanotube films can accommodate relative motions or slip by rolling, sliding, or a combination of rolling and sliding at the interface [19]. However, this mobility related hypothesis seems unlikely considering the degree of nanotube entanglement observed in these films.

The recently found super-compressibility of the vertically aligned nanotube films [20] predicts an order-of-magnitude difference in contact area between the transverse and vertical arrangement. The calculated interfacial shear stresses are nearly the same for both films (0.1–0.2 MPa) indicating that the contact area difference between orientations is a reasonable explanation of the frictional anisotropy. However, the exceptionally low value of predicted shear stress suggests that there are a number of very small intimate contact points supporting load. This is consistent with observed tangled and open morphology of the surface contacting regions (figure 1).

In this study, a series of tribological experiments were performed on vertically aligned and transversely distributed nanotube films using a borosilicate glass countersurface while varying the film temperature from 303–393 K. These experiments had a prescribed 2 mN normal load, 300  $\mu\text{m}/\text{sec}$  sliding speed, and a track length of 600  $\mu\text{m}$ . A total of 100 reciprocating cycles were run in open laboratory air (45% RH) at each temperature. As previously found, the friction coefficient

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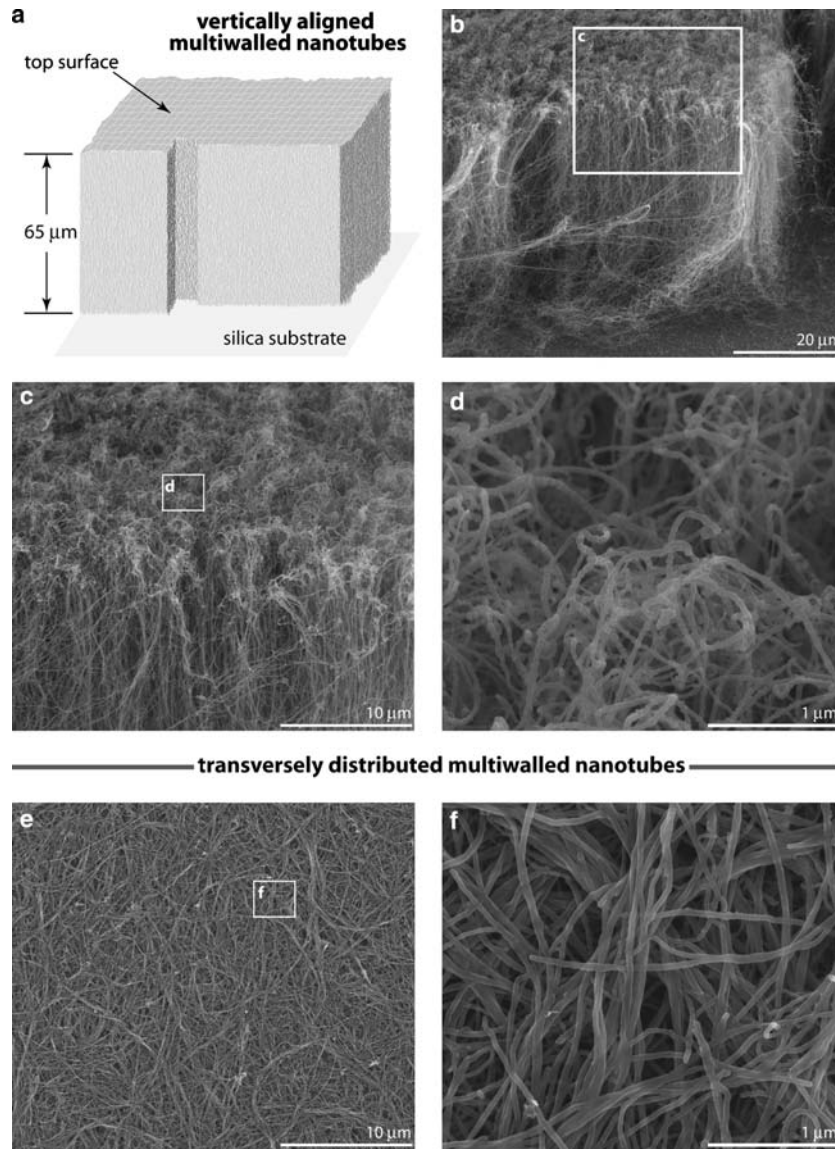


Figure 1. Oriented MWNT film structures. (a) A schematic of an SEM image (b) taken of an exposed edge of the vertically aligned MWNT films. The image is taken at a 52° tilt, and was found to have a characteristic height of 65 μm. Images (c) and (d) are indicated in (b) and (c) respectively. The top surface shown in (d) is typical of the tangled morphology that does not have a preferential vertical orientation, which is clearly visible in (b) and (c). Image (e) is a top view of a transversely distributed sample prepared from the same tubes shown in (b)–(d). This sample was prepared by sonicating mechanically removed tubes in acetone and then drying them onto a quartz sample. Image (f) is a higher magnification of the region indicated in (e).

of the vertically aligned film was approximately ten times higher than the transversely distributed film at 303 K (figure 2(b)). The value at 303 K (the lowest temperature tested) is indicated as  $\mu_o$  for each of the films and was used as a reference friction coefficient in the analysis. As the film temperature was increased there was a monotonic decrease in the friction coefficient. This behavior was completely recoverable and reversible. The friction coefficient of both oriented MWNT films could be tuned by an order of magnitude by simply varying the temperature of the nanotube films. This result demonstrates the potential opportunity to use nanotube films as active surfaces that can provide high friction coefficient or lubricity on demand.

In figure 2(b) it appears that this temperature effect is more pronounced in the vertically aligned films, however, when the friction coefficients are normalized to the 303 K values ( $\mu_o$ ) the relative changes in friction coefficient are nearly the same for the two films. This is shown in figure 2(c) over the range of temperatures examined. For this data set two points were collected at each temperature: one during heating and the other during cooling. An Arrhenius plot of this normalized friction coefficient behavior, shown in figure 2(d), gives an activation energy of  $E_a = 16$  kJ/mol. This value of activation energy is consistent with hydrogen bonding; silica glasses are known to have hydroxy-groups on their surfaces [21], and post-production plasma treatment

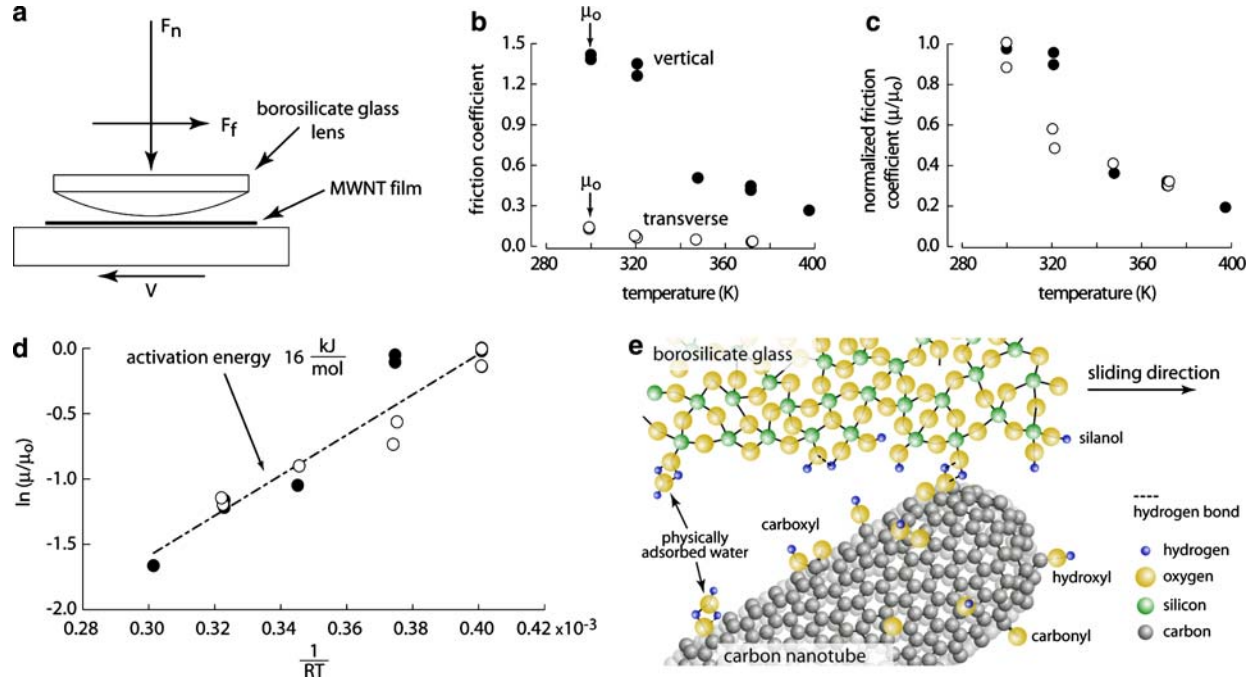


Figure 2. Temperature, orientation, and interface bond dependent friction. (a) The experimental schematic the MWNT films are located on a reciprocating stage the slide under replaceable countersurfaces, the experiments described here were run on a borosilicate glass lens that had an  $\sim 8$  mm radius of curvature, (b) The friction coefficient of the two films versus surface temperature in an open-air environment, (c) The friction coefficient is normalized by the 303 K value revealing that the relative changes for the two films were the same, (d) An Arrhenius plot of the normalized friction coefficient suggesting that hydrogen bond breaking is the dominant contribution to friction coefficient during the interfacial sliding between the MWNT films and the glass counter surface, (e) A schematic of the molecular view inferred from these experiments.

with oxygen moieties shows unambiguous evidence that the functionalization of the nanotube framework includes carboxyls ( $-\text{COOH}$ ), hydroxyls ( $-\text{OH}$ ) and carbonyls ( $-\text{C}=\text{O}$ ) [8–12, 22, 23]. This leads to the molecular view of the contact illustrated in figure 2e, where the frictional response is controlled by the unintentionally attached functional groups on the surface of the glass and the nanotubes suggesting the tribology of these surfaces can be intentionally modified through different chemistries and functionalization.

A relatively simple test of this hypothesis was to repeat tribological experiments using countersurfaces of gold instead of borosilicate glass. Gold surfaces have been well characterized and electron beam evaporation of gold onto the borosilicate glass lens surface gives nearly the same polished finish. The gold coated surfaces are devoid of the  $-\text{OH}$  groups that we hypothesize are responsible for the hydrogen bond dominated friction response. The same experimental protocol was repeated using the gold coated lenses, and was expanded to include lenses of three curvature radii: 7.78, 4.65 and 1.00 mm. The results of these experiments are shown in figure 3 (a). The data show that the friction coefficients are reduced by nearly a factor of two, and the friction coefficients can be further lowered by reducing the radii of curvature, which reduces the nominal contact area. Previous publications [6, 24] demonstrated friction coefficients of the nanotube films are not altered by

changes from open air conditions to inert environments. In this study, the set of experiments with the 1.00 mm gold coated lenses (plotted in figure 3) demonstrate that this temperature effect on friction coefficient is also insensitive to the gaseous environment. The experiments run in open laboratory air had a relative humidity of 45% and the experiments in the argon environment used gases that had a reported purity of less than 5 ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$ .

Normalizing the friction coefficients to the 303 K values ( $\mu_0$ ) shows that the relative changes in friction coefficient with increasing temperature are similar for all gold coated samples and conditions (figure 3(b)). The relative change in friction coefficient with temperature is much less than for the borosilicate glass countersurfaces. The activation energy fit to the gold data set (figure 3(c)) is 3 kJ/mol, which is indicative of van der Waals bond breaking during sliding between the MWNT and the gold [25].

The purification of nanotubes by removing amorphous carbon films through plasma etching is widely used. In order to demonstrate tunable friction coefficient, the vertically aligned MWNT films were treated in a 100 W glow discharge plasma with combinations of argon & nitrogen, and argon & hydrogen. After etching for 45 s, the surfaces were examined with x-ray photoelectron spectroscopy (XPS) (figure 4 (a)–(d)). The C1s peak of the argon & hydrogen treatment (figure 4(b))



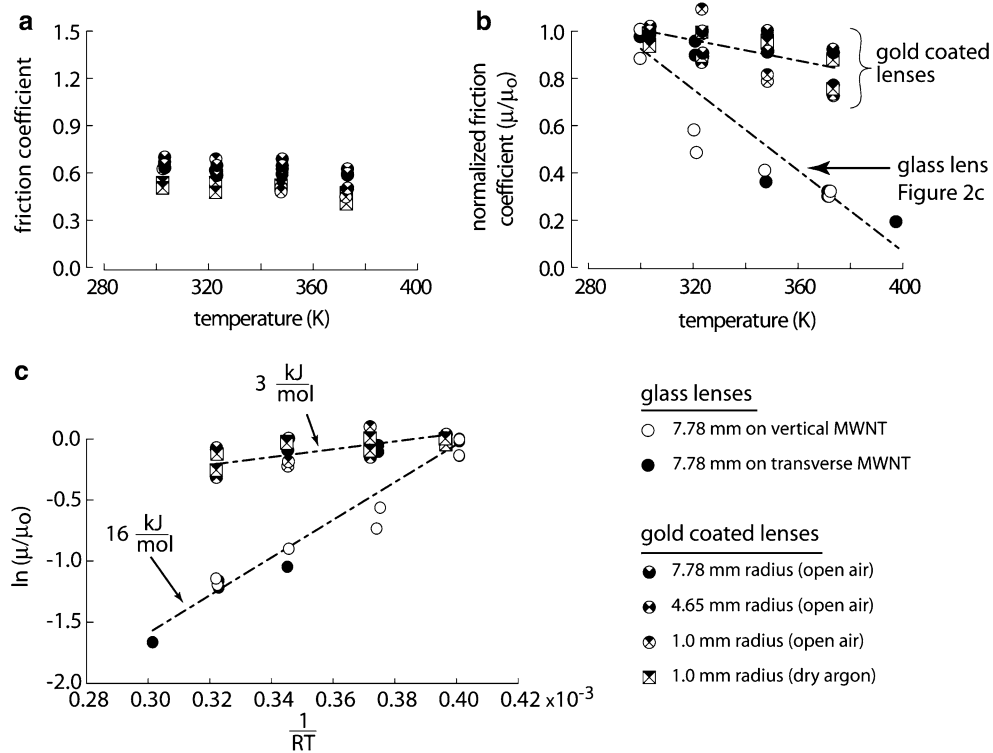


Figure 3. Gold-MWNT sliding interface friction and activation energy. (a) A plot of the friction coefficient for gold coated countersurface conditions against the vertically aligned MWNT film versus surface temperature run on a vertically aligned MWNT film using multiple radii and both laboratory air and dry argon, (b) The friction coefficient is normalized by each 303 K value revealing that the relative changes for all gold countersurface conditions were the same, but was distinctly different than the normalized trend for the borosilicate glass countersurface, (c) An Arrhenius plot of the normalized friction coefficient suggests that hydrogen bond breaking is the dominant contribution to friction coefficient during the interfacial sliding between the MWNT films and the glass counter surface and van der Waals bond breaking is the dominant contribution to friction coefficient when sliding against a gold countersurface.

was slightly broadened in comparison to the untreated sample (figure 4(a)), which is expected with the addition of C-H bonds. From previous XPS studies of hydrocarbons, the C1s peak of C-H bonding is at higher energies as compared to 284.6 eV for C-C bonds in graphite [26] contributing to the C1s peak broadening. The C1s peak broadening was more pronounced for the argon & nitrogen treatment (figure 4(c)), evolving in the direction of higher bonding energies. This is in correspondence to formation of C-N bonds, where C1s bonding energy was reported to vary from 285.9–287.8 eV as a function of carbon atom electron hybridization [27]. For all plasma treated carbon nanotubes, there was no oxygen contamination or C-O bond formation. This is evidenced in figure 4 from the absence of C1s peak features at 290–292 eV which would be typical for thermally oxidized carbon or oxygen plasma treated polymers [28].

Interestingly, the XPS analyses of N1s region for the argon & nitrogen treatment in figure 4(d) presents clear evidence of a doublet structure of the nitrogen atom bonding. This duplet structure of N1s region is exactly the same as the one observed in studies of fullerene-like  $CN_x$  [29, 30]. The possibility of generating fullerene  $CN_x$  structures on the ends of carbon nanotubes in argon &

nitrogen treatment, as hinted by the XPS analyses, is an interesting avenue of further investigations.

When plasma treated nanotubes were tested in sliding against the borosilicate glass surface in open laboratory air, the friction coefficients of both plasma treated films showed a weak dependence on temperature (figure 4(e)). The activation energy fit from both plasma treated MWNT films (figure 4(f)) is 3 kJ/mol. Examination of both the borosilicate glass lens and gold coated pin surfaces after test completion revealed no evidence of transfer film formation. This in combination with the lack of wear on the MWNT film surfaces supports the mechanism of pin-counterface chemical bond activation energy as the dominating frictional mechanism.

This work demonstrates that the friction coefficients can be tuned by tailoring the chemical interfaces between nanotubes and countersurfaces, and the contact temperature. Smart surfaces and multifunctional structures with tunable friction behavior can be designed using multiwalled nanotube films as foundation and tailoring the surface treatments and counterface chemistries for the target application. The ability to reduce the friction coefficient with surface heating (potentially using the nanotubes themselves as the resistive elements) provides a path for dynamic control of the friction

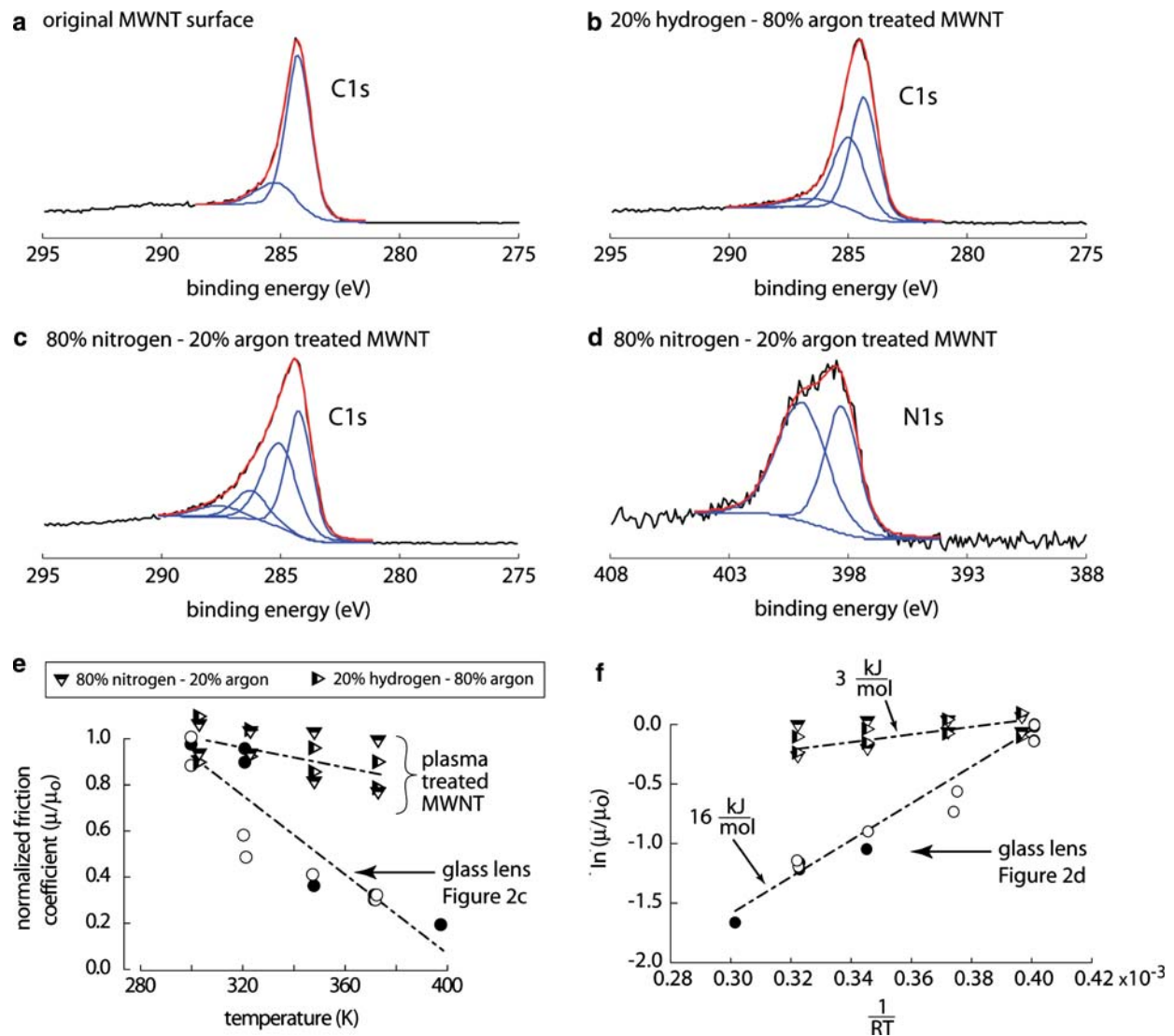


Figure 4. Effects of MWNT plasma treatment on sliding interface temperature dependence. XPS spectra of the carbon 1s peak of MWNT vertically aligned films (a) non-plasma treated, (b) argon & hydrogen plasma treatment, and (c) argon & nitrogen plasma treatment, (d) XPS spectra of the nitrogen 1s region of the of the argon & nitrogen plasma treatment, (e) The friction coefficient normalized by each 303 K value reveals that the nitrogen and hydrogen treatments were successful at removing the temperature sensitivity on friction coefficient, and (f) suggests a shift from hydrogen bonding dominated friction (figure 2d) to van der Waals dominated friction.

coefficient over a wide range of operational environments.

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